

SILICON CARBIDE SINTERED PRODUCTS
AND A METHOD FOR THEIR MANUFACTURING

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16. Abstract SiC-based sinters are produced by pressureless sintering from a SiC-AlN solid solution containing Al 2-20, N 0.2-10, O 0.2-5, a Group IIIB element 0-15 wt-%, the remainder being Si and C. Thus, a 90:10 mixture of SiC and AlN powders was cold-pressed at 2000 kg/cm ² and sintered for 5 h at 2100° in a N atmosphere. The resulting product had d. 3.11 g/cm ³ and bending strength at ambient and 1400° of 68.5 and 66.3 kg/mm ² .			
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PATENT CLAIMS

1. Silicon carbide sinter product characterized by the fact that it is composed essentially of lengthy and/or table-like grains of an SiC-AlN fix solution, consisting primarily of 2 to 20% by weight of Al, 0.2 to 10% by weight of N, 0.2 to 5% by weight of O, and 0 to 15% by weight of a group IIIa element, with the remainder primarily Si and C.
2. Silicon carbide sinter product as per claim 1, characterized by the fact that the average grain size of the grains is less than 10 $\mu\text{-m}$.
3. Silicon carbide sinter product as per claim 1, characterized by the fact that the average grain size of the grains is less than 5 $\mu\text{-m}$.
4. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a density of more than 95% of the theoretical density.
5. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a density of more than 98% of the theoretical density.
6. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a bending strength of more than 60 kg/mm^2 at room temperature, and more than 65 kg/mm^2 at 1400 $^{\circ}\text{C}$.

7. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a bending strength of more than 65 kg/mm^2 at room temperature, and more than 70 kg/mm^2 at 1400°C .
8. Silicon carbide sinter product as per claim 1, characterized by the fact that it contains 3 to 15% by weight of Al, 0.2 to 4% by weight of O, and 0.1 to 10% by weight of a group IIIa element.
9. Silicon carbide sinter product as per claim 1, characterized by the fact that it contains 0.4 to 3% by weight of O.
10. Silicon carbide sinter product as per claim 1, characterized by the fact that it contains 0.5 to 2% by weight of O.
11. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a bending strength of more than 70 kg/mm^2 both at room temperature and at 1400°C .
12. Silicon carbide sinter product as per claim 1, characterized by the fact that it has a bending strength of more than 80 kg/mm^2 both at room temperature and at 1400°C .
13. Silicon carbide sinter product as per claim 1, characterized by the fact that the group IIIa element is at least one element chosen among Y, La and Ce.
14. A method for producing a silicon carbide sinter product which is composed essentially of lengthy and/or table-like grains of an

SiC-AlN-fix solution, characterized by the fact that the preparation consists of:

(a) Mixing

1. 50 to 97% by weight SiC powder
2. 3 to 30% by weight AlN powder
3. 0 to 15% by weight of a source for a group IIIa element, and
4. 0 to 20% by weight of at least one member of a group composed of a source for SiO_2 , a source for Al_2O_3 and Si_3N_4 , to form a starting mixture which is a source for refractory starting material, computed as refractory starting material;

(b) shaping the mixture in a shaping step to create a rough blank; and

(c) sintering the blank in a sintering step in a non-oxidizing atmosphere at a temperature of 1900 to 2300 °C.

15. A method as per claim 14, characterized by the fact that the sintering is performed for 1 to 24 hours.

16. A method as per claim 14, characterized by the fact that the non-oxidizing atmosphere contains a vapor of Al and/or an Al-compound.

17. A method as per claim 16, characterized by the fact that the rough blank is sintered together with a powder and/or granular mass of AlN, surrounding the blank.

18. A method as per claim 16, characterized by the fact that the rough blank is sintered together with a powder mixture of Al_2O_3 and SiC and/or C or a powder mass of some similar mixture, surrounding the blank.

19. A method as per claim 14, characterized by the fact that the pressure of the non-oxidizing atmosphere is 0.5 to 1.5 atm.

20. A method as per claim 14, characterized by the fact that the non-oxidizing atmosphere contains N_2 as main component and its pressure is 2 to 50 atm.

21. A method as per claim 14, characterized by the fact that the mixture contains 60 to 96.3% by weight of SiC powder, 3 to 25% by weight of AlN-powder, and 0.2 to 15% by weight of a source for a group IIIa element.

22. A method as per claim 14 characterized by the fact that the mixture contains 0.5 to 20% by weight of at least one member of a group consisting of a source for SiO_2 , a source for Al_2O_3 and Si_3O_4 .

23. A method as per claim 21 characterized by the fact that the mixture contains 0.5 to 20% by weight of at least one member of a group consisting of a source for SiO_2 , a source for Al_2O_3 and Si_3O_4 .

24. A method for producing a silicon carbide sinter product which is composed essentially of lengthy and/or table-like grains of an SiC-AlN fix solution, characterized by

- a) A process step of mixing of sources for refractory starting materials to form a mixture, which, computed as refractory starting materials, contains (1) 50 to 97% by weight SiC powder, (2) 3 to 30% by weight AlN powder, (3) 0 to 15% by weight of a source for a group IIIa element, and (4) 0 to 20% by weight of at least one member of a group consisting of a source for SiO₂, a source for Al₂O₃ and Si₃N₄;
- b) A process step of shaping the mixture to create a rough blank;
- c) A process step of sintering the rough blank in a non-oxidizing atmosphere at a temperature of 1900 to 2300 °C; and
- d) A process step of treatment of the sinter body in a non-oxidizing atmosphere under a pressure of 20 to 3000 atm. at a temperature of 1900 to 2300 °C.

25. A method as per claim 24, characterized by the fact that the sinter body is treated in an atmosphere under a pressure of 50 to 200 atm.

26. A method as per claim 24, characterized by the fact that the sinter body is treated in an atmosphere under a pressure of 500 to 2000 atm.

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Silicon Carbide Sinter Product and Method for its Production

The present invention pertains to silicon carbide sinter products and to a method for their production. In particular, the invention concerns a silicon carbide sinter product composed essentially of a SiC-AlN-fix solution, which has a high density and a high strength, even at high temperatures. The product can even be produced by pressureless sintering of a rough blank.

Similar to sinter products of silicon nitride, the silicon carbide sinter products are intended as possible ceramic building materials. A number of proposals have been made which relate to such silicon carbide sinter products, and to their production. As methods for example, a reaction sinter method, a hot press method or a pressureless sinter method can be mentioned. In the reaction sinter method, metallic silicon is impregnated for example, into a carbon-containing rough blank, and the whole is held at its reaction temperature to form a silicon carbide sinter product. This method makes it possible to produce any type of complex shaped sinter products. But a disadvantage of this method is that the strength drops off quickly at a temperature of about 1400 °C. In the hot press method, a small quantity of a boron compound, aluminum metal or an aluminum oxide is mixed with silicon carbide powder, and the mixture is treated at high temperature under high

pressure in a mold. In this manner, a sinter product is obtained which has in general a high strength and a high density, compared with sinter products obtained by reaction sintering, or by pressureless sintering. But in order to use the products obtained by hot pressing as high temperature building materials, e.g. as parts in a gas turbine or such, and to be able to utilize the superior properties of silicon carbide, e.g. heat resistance, oxidation resistance and alternating temperature resistance at high temperatures, it is necessary that there be a high strength, not only at room temperature, but also at high temperatures. Hot-pressed products which meet these requirements are being developed at this time. For example, hot pressed silicon carbide products having high strength even at high temperatures, have been proposed in JA-OS 47275/1980. This publication presents a sinter product composed exclusively of a specially treated silicon carbide powder. The JA-OS 67572/1980 describes a silicon carbide sinter product which contains aluminum nitride and/or boron nitride. JA-OS 92168/1981 describes a silicon carbide sinter product which contains a magnesium source, and JA-OS 92169/1981 describes a silicon carbide sinter product which contains a beryllium component, a boron component or an aluminum component. All these sinter products are produced by hot pressing, and are thus restricted to simple configurations. Due to the disadvantage that they cannot be put into any, desired shape, these materials are not entirely satisfactory with regard to their use as construction ceramics.

In the pressureless sinter method, a suitable sinter aid is incorporated. In this manner, a rough blank of silicon carbide powder--which normally will hardly sinter--can be sintered under atmospheric pressure conditions, or under an overpressure which approximates atmospheric pressure. With this method it is possible to obtain extremely dense, high-strength sinter products with any desired shape. The strength of the products, especially their high-temperature strength, is still insufficient, and there are other disadvantages. Refer to JA-OS 42577/1982 which describes a silicon carbide sinter product which was obtained by pressureless sintering under addition of a small quantity of aluminum oxide. Its bending strength at 1400 °C amounts to 58 kg/mm² at best. Conversely, JA-OS 88079/1982 describes a silicon carbide sinter product which is obtained by pressureless sintering, under addition of carbon-containing material. It has a bending strength of about 71 kg/mm² at 1200 °C. But this product requires a siliconizing treatment, in conjunction with the pressureless sintering. Moreover, it is assumed that this product has the disadvantage--like products obtained by reaction sintering--that the strength drops off quickly at a temperature of about 1400 °C.

Sinter products composed of a mixture of SiC and AlN have already been described.

As per JA-OS 3396/1980, a mixture of SiC powder and AlN-powder is pressureless sintered, or the SiC powder is sintered in an AlN-atmosphere at atmospheric pressure, in order to obtain a

sinter product from a mixture of SiC and AlN. In the production of this sinter product, carbon or a carbon source is incorporated into the SiC powder and the density of the sinter product amounts to 93.3% at best.

In US PS 4,230,497 (JA-OS 118411/1979) an alpha-SiC sinter product is described which contains a small quantity of aluminum and additional carbon, which is obtained by pressureless sintering of SiC powder under addition of a small quantity of an aluminum source, like AlN, together with a carbon source. This sinter product contains only 0.1% by weight of oxygen, and the high-temperature bending strength of this sinter product amounts to only 640 N/mm^2 (i.e. 65 kg/mm^2). In addition, with this production method it is difficult to disperse a small quantity of the carbon sources uniformly in the starting material.

In US PS 4,326,039 (JA-OS 9277/1981) or JA-OS 167179/1980 a beta-SiC sinter product or an alpha-SiC sinter product is described, which contains a small amount of aluminum, which is obtained by hot pressing of SiC powder which contains a small quantity of an aluminum source, like Al or AlP. But again, it was stressed that the oxygen content has to be kept to a minimum. The high-temperature strength of sinter products obtained in this manner amounts to only 670 N/mm^2 (i.e. 68 kg/mm^2). Moreover, a silicon carbide sinter product of this type has poor strength properties similar to a pressureless sintered silicon carbide product containing boron and carbon, and it has another consider-

able disadvantage that it can easily flake during its use or processing.

Most recently, work has begun on investigating sinter products of SiC-AlN fix solutions.

Rafaniello et al. reported that SiC-AlN fix solution powders were produced from $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, starch and fine SiO_2 powder as starting materials, and that by addition of a small quantity of carbon, a sinter product was obtained from the SiC-AlN fix solution [J. Materials Sci. 16 (1981), 3479]. These sinter products were produced by a hot press method, and it is assumed that their microstructure is composed primarily of same-axis (equiaxial) grains. Such sinter products do not fulfill the purposes of the present invention, however.

Ruh et al. reported that a sinter product is obtained from an SiC-AlN fix solution by hot pressing a mixture of beta-SiC powder and AlN powder in a vacuum [J. m. Chem. Soc. 65 (1982), 260]. However, this sinter product has a microstructure which is built of equiaxial grains, and its bending strength at room temperature is as low as 17 to 27 kg/mm^2 .

The inventors performed extensive investigations with the goal of obtaining a silicon carbide sinter product with the desired properties, so that instead of hot pressing, a pressureless sinter method could be used, and so its properties are equal to or better than those of a product obtained by hot pressing. In this regard, various proposals had already been made. It turned out that a silicon carbide sinter product containing a specific

quantity of AlN, and a specific quantity of a group IIIa element oxide can be produced by a pressureless sinter method, and that the obtained sinter products will have excellent properties, especially with regard to strength and density. In further tests, the microstructure of such a silicon carbide sinter product were set forth. It was found that a silicon carbide sinter product containing specific quantities of aluminum, nitrogen and oxygen has the desired properties. The present invention is based on the results of these investigations.

Accordingly, a silicon carbide sinter product is created which is composed essentially of lengthy and/or table-like grains of a SiC-AlN fix solution, which consists essentially of 2 to 20% by weight of Al, 0.2 to 10% by weight of N, 0.2 to 5% by weight of O, 0 to 15% by weight of a group IIIa element, with the remainder being primarily Si and C.

The invention is explained below by using a preferred design.

Figure 1 shows a scanning electron microscope photograph of the microstructure of the sinter product obtained in example 6. Figure 2 likewise presents a scanning electron microscope photograph of the microstructure of the sinter product obtained in example 7.

The invented sinter product is composed primarily of lengthy (elongated) and/or table-like grains. By elongated or table-like grains, in this regard we mean those crystalline grains having a L/R ratio of at least 3/1, where L represents the length of a grain, and R the smallest diameter of the grain, determined in a

plane which forms a right angle with the length, at the center of the length of the grain, when viewed three-dimensionally. But in practice, grains are viewed two-dimensionally, through microscopic observation of the polished cut surface of the invented sinter product. In this type of two-dimensional consideration, such grains belong to the elongated or table-like grains as per this invention, provided they have an L'/R' ratio of at least $3/1$, where L' stands for the length of the particular grain, and R' stands for the diameter of the grain, determined along a line forming a right angle with the length in the center of the length of the grain. In case the invented sinter product is subjected to a two-dimensional consideration in this manner, the number of grains with an L'/R' ratio of at least $3/1$ will amount to at least $1/3$, preferably at least $1/2$, related to the total number of grains.

The greater the L/R ratio, the better the mechanical properties of the sinter product. Similarly, the strength of the sinter product improves, the greater the percentage of grains with an L/R -ratio of at least $5/1$. Accordingly, it is particularly preferred if the number of grains with an L'/R' ratio of at least $5/1$ is $1/2$, related to the total number of grains.

The average grain size, defined as the average value of L' , is preferably less than $10\text{ }\mu\text{m}$. Thus, the strength of the sinter product is improved. The average grain size is particularly preferred to be less than $5\text{ }\mu\text{m}$, which will cause a further, notable improvement in strength. The microstructure of the sinter

product has an effect not only on improving the strength, but also with regard to improving the toughness.

The grains consist of an SiC-AlN fix solution, where an atomic ratio of Si/C of about 1 is present, and an atomic ratio of Al/N of about 1 or more in many cases, is created. The grains can contain small quantities of oxygen and/or group IIIa elements, in addition to the above named four elements.

At the grain boundaries of the grains there exists a grain boundary phase, which is assumed to contain Si, Al, O, N and C, and which in some cases also contains group IIIa elements. It is assumed that the main quantities of oxygen and group IIIa elements are present in the invented sinter product in this grain boundary phase. This grain boundary phase can be glass-like. But preferably it is crystalline, which leads to an improvement in the high-temperature strength of the sinter product. If the grain boundary phase contains group IIIa elements, then the softening temperature of the grain boundary phase tends to be too high, and it is assumed that the high-temperature strength is thereby improved.

The theoretical density of silicon carbide is 3.21. Now if an additional component is present, a corresponding change in theoretical density occurs to a certain extent. In the invented sinter product, the density is greater than 90% of the theoretical density. Moreover, with the invention it is easily possible to obtain a significantly dense sinter product which has a density

greater than 95%, especially greater than 98%, of the theoretical density.

The invented sinter product contains 2 to 20% by weight of Al, 0.2 to 10% by weight of N and 0.2 to 5% by weight of O as the essential components of the chemical composition. Furthermore, it can contain less than 15% by weight of group IIIa elements as insignificant components. The remainder is composed essentially of Si and C, where the main quantity of these elements is present in the form of an SiC-AlN fix solution.

The invented sinter products can be composed exclusively of Si, C, Al, N, O and group IIIa elements. However, they can also contain other elements in minor quantity, e.g. at most 1% by weight, as long as the properties of the invented sinter product are not thereby reduced.

An important characteristic of the invented sinter product is that it contains a specific quantity of oxygen. In the conventional sinter products of silicon carbide, the presence of oxygen is viewed as an obstacle to achieving a high density or high strength. Due to the fact that the surface of the silicon carbide powder used as starting material is unavoidably oxidized to silicon oxide, it has been assumed that the purity is affected and that therefore such oxidation should be prevented. In order to prevent the sinter product from containing such oxide, commonly carbon or a carbon source convertible into carbon, was added to the starting material. Conversely, in the invented sinter products, the presence of oxygen is a significant property.

Consequently, a silicon carbide powder which is not necessarily highly pure, i.e. one which contains an oxide, like silicon oxide, can be used as starting material. Another advantage is that the incorporation of carbon or of a carbon source--which represents a troublesome process step--is not necessary.

The total quantity of Al and N in the invented sinter product should be 4 to 20% by weight, especially 5 to 15% by weight, related to the sinter product. Thus, a sinter product is obtained which is composed of grains having a high L/R-ratio and a small average grain size, and whose strength is high.

The invented sinter product, which contains no group IIIa elements, has a bending strength greater than 60 kg/mm^2 at room temperature and at 1400°C . In this case, it is preferred to have Al 5 to 15% by weight, N 0.4 to 10% by weight, and O 0.4 to 3% by weight, which gives a particularly high bending strength at 1400°C , or specifically greater than 65 kg/mm^2 .

Now if the sinter product contains a group IIIa element, the strength at room temperature and at high temperatures is improved over the sinter product not containing a group IIIa element. Particularly preferred is a sinter product containing 3 to 15% by weight Al, 0.2 to 10% by weight of N, 0.2 to 4% by weight of O, and 0.1 to 10% by weight of a group IIIa element. In this composition, the bending strength at room temperature and at 1400°C is greater than 70 kg/mm^2 , or even greater than 80 kg/mm^2 .

By group IIIa elements in this regard, we mean at least one element selected from the group Sc, Y and elements with an atomic

number of [illeg.] to 71 and 89 or greater. Among them, at least one element selected from Y, La and Ce, is preferred, since in this case the starting materials are easily obtained, and the chemical stability of the sinter product is good.

Moreover, it is preferred that the sinter product contain 0.4 to 3% by weight of O, which causes a large L/R grain ratio, and the density of the sinter product is likewise high. Particularly preferred is a sinter product containing 0.5 to 2% by weight of O. Now here, the L/R ratio is greater than 5 and the density of the sinter product is greater than 98% of the theoretical density.

The silicon sinter product which is composed essentially of elongated and/or table-like grains of an SiC-AlN fix solution, and which has a high density and superior mechanical properties, can be obtained by a process which comprises the following process steps.

(a) A process step which mixes sources for refractory starting materials to form a mixture, which contains (1) 50 to 97% by weight of SiC powder, (2) 3 to 30% by weight of AlN powder, (3) 0 to 15% by weight of a source for a group IIIa element, and (4) 0 to 20% by weight of at least one member of a group composed of an SiO_2 source, an Al_2O_3 source and Si_3N_4 , source computed as refractory starting materials;

(b) A process step of shaping the mixture in order to obtain a rough blank, and

(c) A process step of sintering the rough blank in a non-oxidizing atmosphere at a temperature of 1900 to 2300 °C.

By refractory starting materials we mean in this regard, refractory components which remain when the sources for the refractory starting materials are treated at a high temperature, e.g. 1000 °C. The same is basically also true with regard to the SiC powder, AlN powder, metallic Yttrium and such, the sources for refractory starting materials, and the refractory starting materials themselves. Now if, for example, lanthanum hydroxide, $\text{La}(\text{OH})_3$ as source for a group IIIa element, or aluminum ethoxide, $\text{Al}(\text{OC}_2\text{H}_5)_3$, as source for Al_2O_3 , is used as source for the refractory starting material, then lanthanum oxide, La_2O_3 , or aluminum oxide, Al_2O_3 corresponds to the refractory starting material. Regarding the quantity ratios of sources for the refractory starting material, as specified below, we are dealing with quantity ratios which were computed on the basis of corresponding refractory starting materials, and to be sure, related to the total quantity of refractory starting materials.

The average particle size of the SiC powder should be at most 5 μm . thus, a sinter product can be obtained which has a density greater than 95% of the theoretical. Particularly preferred is an average particle size of at most 1 μm . In this case, a sinter product with an even greater density is obtained.

The crystalline form of SiC powder can be either an alpha- or beta-form. But the beta-form is preferred, since in this case the proportion of elongated and/or table-like grains tends to increase, and the L/R-ratio tends to higher values.

For the same reasons as in the case of the SiC powder, it is preferred that each of the components, AlN powder, source for the group IIIa element, source for the SiO_2 , source for Al_2O_3 and Si_3N_4 be present in the form of a powder with an average particle size of at most 5 $\mu\text{-m}$, preferably max. 1 $\mu\text{-m}$.

The essential components used as sources for the refractory starting material in the production of sinter products, are SiC powder and AlN powder. In a typical design form, a mixture can be used which consists essentially of 70 to 97% by weight of SiC powder, and 3 to 30% by weight of AlN powder as the sole sources for refractory starting material. In general, the SiC powder and the AlN powder exhibit oxidized surfaces. Thus, these materials do not contain negligible quantities of SiO_2 or Al_2O_3 . Consequently, a sinter product obtained from these sources for refractory starting material, generally contains at least 0.2% by weight of oxygen and in most cases, 0.2 to 2% by weight of oxygen.

If the AlN powder amounts to less than 3% by weight, or if the SiC powder is present in a greater quantity than 97% by weight, then the average grain size of the grains of the sinter product tends to increase, whereas the L/R ratio tends to decrease. Thus, the proportion of equiaxial grains increases and the density and bending strength decrease. If on the other hand, the AlN powder amounts to more than 30% by weight, or if the SiC powder amounts to less than 70% by weight, then the bending strength of the sinter product becomes small and the thermal

coefficient of expansion then tends to increase. This leads to a decrease in the alternating temperature resistance of the sinter product.

In the case described above, the mixture of the sources for refractory starting material should contain 75 to 95% by weight of SiC powder and 5 to 25% by weight of AlN powder. In this manner, a sinter product with greater strength can be obtained.

As per another, preferred design, the mixture of sources for refractory starting material used in production of the sinter product, contains 60 to 96.8% by weight of SiC powder, 3 to 25% by weight of AlN powder, and 0.2 to 15% by weight of a source for a group IIIa element. In this case, the sinterability is improved, so that a sufficient density and strength are obtained at a lower sinter temperature, or after a shorter sinter time. Particularly preferred is a mixture containing 70 to 95.8% by weight of SiC powder, 4 to 20% by weight of AlN powder, and 0.2 to 10% by weight of a source for a group IIIa element. In this case, a sinter product is obtained whose density is greater than 98% of the theoretical density, under sinter conditions of 2000 to 2200 °C for 2 to 15 hours. The bending strength at room temperature and at 1400 °C is exceptionally high; greater than 70 kg/mm².

A source for the group IIIa element can be in this regard, simple substances or compounds of the above mentioned group IIIa elements or their mixtures. As compounds of group IIIa element, their oxides are preferred, or oxide sources for group IIIa elements, like hydroxides, oxylic acids or organic acid salts.

These components cause the formation of a liquid phase with a high melting point and a high viscosity, during the sintering.

Sintering of the liquid phase and the formation of a solid solution with a desired microstructure are simplified and the starting materials are easily obtained. In addition, when using carbides, nitrides or silicides of group IIIa elements, or their mixtures, the high-temperature strength is increased.

According to the invention, a desired sinter product is obtained from a mixture of sources for refractory starting material, including SiC powder and AlN powder as essential components, and a source for a group IIIa element as facultative component. The mixture of sources for refractory starting material can also contain as facultative component, a specific quantity of at least one member of the group composed of a source for SiO_2 , a source for Al_2O_3 and Si_3N_4 .

If the mixture of sources for refractory starting material consists essentially only of SiC powder and AlN powder, then the oxygen content in the sources for refractory starting material is low, i.e. from 0.5 to 2% by weight. In such a case, by addition of a source for SiO_2 and/or a source for Al_2O_3 , the formation of the liquid phase can be promoted during the sintering, and the sintering of the liquid phase and the formation of the solid solution can be simplified, which will improve the density and strength of the sinter product. It is an advantage if the source for SiO_2 and/or the source for Al_2O_3 is incorporated in a quantity of 0.5 to 10% by weight of the mixture of sources for refractory

starting material. When a quantity less than 0.5% by weight is used, then the above effects are small. If on the other hand, the quantity exceeds 10% by weight, then the strength of the sinter product tends to decline.

If the mixture of sources for refractory starting material includes SiC powder, AlN powder and an oxide source of the group IIIa element, then the oxygen content in the sources for refractory starting material should be 0.5 to 5% by weight. In this case it is also preferred to incorporate 0.5 to 5% by weight of the source for SiO_2 and/or of the source for Al_2O_3 into the mixture, in order to achieve the same purpose and the same effect as mentioned above.

To improve the strength of the sinter product, it has proven effective to incorporate 0.5 to 15% by weight Si_3N_4 into the mixture of sources for refractory starting material. If this quantity is less than 0.5% by weight, then an insufficient improvement is achieved. On the other hand, if this quantity exceeds 15% by weight, then the strength of the sinter product tends to decrease.

Furthermore, it is also possible to incorporate both the source for SiO_2 and/or the source for Al_2O_3 and also Si_3N_4 into the mixture of sources for refractory starting material. But the total quantity should be less than 20% by weight. If the source for SiO_2 , the source for Al_2O_3 and Si_3N_4 are incorporated into the sources for the refractory starting material, then the critical

value of the SiC powder content can be varied, depending on the particular case.

In summary, we find that the mixture of sources for refractory starting material, computed as refractory starting material, consists of 50 to 97% by weight of SiC powder, 3 to 30% by weight of AlN powder, 0 to 15% by weight of a source for a group IIIa element, and 0 to 20% by weight of at least one member of the group consisting of a source for SiO_2 , a source for Al_2O_3 and Si_3N_4 .

Among the sources for SiO_2 and Al_2O_3 in this regard, are compounds capable of building up SiO_2 or Al_2O_3 , by which we are dealing with refractive starting materials. The expression also includes mixtures of these compounds. As such compounds, not only oxides like SiO_2 itself or Al_2O_3 itself, can be used, but also hydroxides, hydrates or alkoxides, like sulfates or nitrates, or salts of organic acids.

For the above reasons, the group IIIa element should be at least one member chosen from the group Y, La and Ce.

The sources for refractory starting material of the invention can be exclusively composed of SiC powder, AlN powder, a source for a group IIIa element, a source for SiO_2 , a source for Al_2O_3 and Si_3N_4 . However, they can also contain a small quantity, i.e. at most 1% by weight, of sources of other refractory starting materials, up to an amount which does not cause any reduction in the invention effect.

In accord with the invention, the above-mentioned sources for refractory starting material are uniformly mixed, both with and without addition of mixing additives which are not sources of refractory starting material. When using a jet molding process or an extrusion method, an organic resin, like polystyrene or polypropylene, can be used as additive. If an injection molding method is used, then a binder like polyvinylalcohol or carboxymethyl cellulose can be used. In order to obtain a sinter product with high density and good mechanical properties, it is important to mix thoroughly the starting materials to form a homogeneous mixture, e.g. via wet grinding in a ball mill.

In this regard it should be mentioned that in the present invention, the mixture can contain additives like the organic materials mentioned above; they essentially disappear at low temperatures before the sintering takes place. An addition of carbon or of a carbon source, like a phenol resin, is not only unnecessary, but also undesired, since such carbon or carbon source easily leads to disadvantageous effects. More precisely, the oxides in the refractory starting materials are reduced by the carbon when using high temperatures, and this carbon thus acts to remove oxygen. Thus, the substances in the liquid phase which are necessary for liquid phase sintering, are reduced or removed.

Next, the mixture described above is shaped in order to obtain a rough blank. As shaping method, any process can be used which is normally used for shaping ceramics. Primary suitable

shaping methods are in particular pressing, dross casting, injection molding or extruding.

Next, the rough blank is sintered in a non-oxidizing atmosphere at a temperature of 1900 to 2300 °C.

In accord with the above mentioned references, Rafaniello et al. or Ruh et al. proposed that the oxygen content be eliminated by incorporating carbon into the sources for refractory starting material, followed by hot pressing under atmospheric pressure or by hot pressing in a vacuum, in order to obtain a sinter product from a SiC-AlN fix solution. In any case, the sinter product has a microstructure composed primarily of equiaxial grains, and the physical properties of the sinter product are not entirely satisfactory.

A new method for producing high-density, high-strength sinter products is proposed by the inventors; these products will have the above-mentioned microstructure. In this method, quite in contrast to previously recommended removal of the oxygen from the sources for refractory starting material, a certain, specific quantity of oxygen is consciously incorporated and by using a liquid phase forming at the sinter temperature, the liquid phase sintering and formation of the fix solution is promoted.

In accord with the present invention it is possible to use hot pressing in the sintering. But there is one particular advantage that a sinter method can be applied which requires no mould at all, e.g. a pressureless sinter method as typical example. Sinter products with excellent mechanical properties can

be obtained. With regard to the mechanism producing such an excellent effect, there are as yet no clear conceptions. However, it is assumed that the presence of the liquid phase forms uniform, fine-crystalline grains, without them being subject to an excessive crystal growth. Furthermore, the reaction to form the fix solution proceeds at a low temperature. In addition, it is assumed that due to the fact that no mechanical pressure is used, grains with a large L/R ratio are easily formed, and that the low-melting, liquid phase is easily decomposed during the sintering, which causes formation of a grain boundary phase with a good high temperature property. Furthermore, pressureless sintering is exceptionally suitable for mass production of large dimension or complicated-shape sinter products.

The sinter temperature should be 1900 to 2300 °C. More precisely, at a temperature of less than 1900 °C, an insufficient density or insufficient formation of the fix solution occurs. If on the other hand the temperature exceeds 2300 °C, then the SiC or other components are increasingly decomposed, which means that the desired, high-density sinter product cannot be obtained. The sintering temperature should be between 2000 to 2200 °C. In this range, the above-mentioned difficulties can certainly be avoided.

The sintering time should be 1 to 24 hours, especially 2 to 15 hours. If the sintering time is too long or too short, then the same difficulties occur as in the case of excessive or insufficient sintering temperature.

In the sintering step, a non-oxidizing atmosphere is used. Thus, undesirable reactions, like oxidation of SiC or AlN can be suppressed. A suitable atmosphere can be one composed primarily of at least one member of the group N_2 , Ar, He, CO, H_2 and NH_3 . It is expedient to use an atmosphere composed primarily of N_2 , Ar, He or a mixture of them.

Particularly preferred is an atmosphere composed primarily of N_2 , since it is not only inexpensive and safe, but also serves to prevent the decomposition of AlN in the rough blank. Thus, the nitrogen content in the sinter product and the high-temperature strength is effectively increased. For this purpose, the pressure of the non-oxidizing atmosphere, which consists primarily of N_2 , is held preferably at a level of 2 to 50 atm, especially preferred is 5 to 40 atm. At insufficient pressure, the effectiveness with regard to preventing the decomposition of AlN is low, and at excessive pressure, it is difficult to improve the density.

The AlN component in the sources for refractory starting material is relatively susceptible to decomposition or vaporization at the sinter temperature. In many cases, it is preferred to use a non-oxidizing atmosphere with a content of a vapor of Al and/or an Al-compound, in order to counteract the decomposition or vaporization of AlN. To produce such an atmosphere it is preferred to sinter the rough blank together with a powder and/or an AlN mass surrounding the rough blank. As such a mass one can use e.g. shaping bodies or sinter bodies of AlN, or

their fragments. For example, a crucible of AlN can be used, whereby the rough blank is placed inside, or the inside lining of the sinter furnace can consist of AlN. When using AlN powder, the rough blank for sintering can be embedded in the powder.

Furthermore, instead of AlN, a powder mixture of Al_2O_3 and SiC, Al_2O_3 and C, or Al_2O_3 , SiC and C, or clumps produced from such a powder mixture, can be used similarly.

One of the characteristics of the present invention consists in the fact that the sintering can be performed without the use of mechanical pressure via a mold, as in the case of a hot pressing method. Another advantageous property consists in the fact that the pressure of the non-oxidizing atmosphere during the sinter stage is held at a level of 0.5 to 1.5 atm, which renders the use of a gas pressure furnace unnecessary. The invented method is thus suitable for mass production of large-dimension products.

On the other hand, as mentioned above, when using a non-oxidizing atmosphere composed primarily of N_2 , in accord with another, advantageous property, the pressure of the atmosphere is kept at a level of 2 to 50 atm. It is also preferred to treat the sinter product obtained in this manner in a non-oxidizing atmosphere sinter stage at a pressure of 20 to 3000 atm at a temperature of 1900 to 2300 °C. Through such treatment it is possible to eliminate pores in the sinter product, which gives a sinter product whose density is essentially equal to the theoretical density. Consequently, in this way the strength and chemical resistance of the sinter product is increased. It is

preferable if such treatment is conducted at a pressure of 50 to 200 atm. This can be done by using a gas pressure furnace. In this case it is possible to obtain a sinter product with a density greater than 99% of the theoretical density.

In accord with another, preferred design of this treatment, the pressure is maintained at a level of 500 to 2000 atm. This can be effected through the use of e.g. an isostatic hot press. In this case, a sinter product can be obtained whose density is greater than 99.5% of the theoretical density.

The invention is explained below on the basis of examples, without however, restricting the invention in any way.

Examples and Comparison Examples

Table 1 presents the tests numbered 1 to 13 of invention examples, and tests 14 to 17 are for comparison.

In each test, a mixture of sources for refractory starting material identified in table 1, is reacted with ethyl alcohol and thoroughly mixed in a ball mill to obtain a homogeneous mixture. As SiC powder, beta-SiC powder with a min. 98% purity is used; it has an average particle size of max. 1 $\mu\text{-m}$ (excepting tests no. 3 and 13, where alpha-SiC powder of the same purity and the same average particle size is used). The other sources for refractory starting material have a purity of at least 95% and an average particle size of about 2 $\mu\text{-m}$ or less.

The obtained, homogeneous mixture is shaped under hydraulic pressure of 2000 kg/cm^2 to form a rough blank measuring 20 x 20 x

40 mm. This blank is sintered in the gas atmosphere identified in table 1 under atmospheric pressure (excepting test no. 4, where the pressure was 20 atm), under the sinter conditions specified in table 1, to obtain a sinter product. For each of tests no. 5 and 11, the rough blank is sintered while embedding it in AlN powder. In each of tests no. 1, 3 and 13, the rough blank is sintered while embedding it in a powder mixture of Al_2O_3 powder and SiC powder. In test no. 10, the sinter product is post-treated in a nitrogen atmosphere of 100 atm at 2000 °C for 2 hours. In test no. 11, the sinter product is post-treated in a nitrogen atmosphere for 2 hours at 2000 atm and 2050 °C.

The density and bending strength of the particular sinter product or treated product are likewise given in table 1. The bending strength is the three-point bending strength, determined at room temperature and at 1400 °C on a sample measuring 3 x 3 x 30 mm, which was cut out from the sinter product.

A shift is noticed in the signal of SiC in the x-ray diffraction patterns of sinter products of tests no. 1 to 13. Furthermore, from TEM (transmission electron microscope) observations on thin samples of the sinter products of tests no. 1 to 13, it follows that in addition to Si and C, Al and N are present in the main grains. Thus, we find that the main grains all consist of a fix solution of SiC-AlN. From the scanning electron microscope observation of the sinter products of tests no. 1 to 13, it follows that a microstructure is present which is built up primarily of elongated and/or table-like grains. In

figures 1 and 2 we see microscopic photographs of the sinter products of tests no. 6 and 7. The figures show that the sinter products of tests no. 6 and 7 have an average grain size of 5 $\mu\text{-m}$ or 3 $\mu\text{-m}$, respectively. We see that in every case, the sinter product is composed primarily of elongated and/or table-like grains with an L'/R' ratio of at least 7.

The chemical composition of representative sinter products was analyzed. The results are presented in table 2.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
90	85	90	75	88	94	89	80	82	94.5	89	88	68	97.5	60	88	85
10	15	5	20	10	5	10	15	10	5	10	10	22	0.5	35	7	-
-	-	-	-	-	Y ₂ O ₃ 1	Y ₂ O ₃ 1	CeO ₂ 5	Y ₂ O ₃ 8	Y ₂ O ₃ 0.5	Y ₂ O ₃ 1	Y ₂ O ₃ 1	La ₂ O ₃ 5	Y ₂ O ₃ 2	Y ₂ O ₃ 5	Yb ₂ O ₃ 25	Y ₂ O ₃ 5
-	-	5	-	-	-	-	-	-	-	-	-	3	-	-	-	10
-	-	-	5	-	-	-	-	-	-	-	-	2	-	-	-	-
-	-	-	-	2	-	-	-	-	-	-	1	-	-	-	-	-
2100	2100	2050	2000	2100	2100	2100	2050	2100	2050	2050	2100	2000	2150	2050	3000	2000
5	5	5	10	5	5	5	5	5	5	5	10	5	2	2	3	8
N ₂	N ₂	N ₂	N ₂	N ₂	Ar	N ₂	Ar	N ₂	Ar	N ₂	N ₂	Ar	N ₂	Ar	N ₂	Ar
3.11	3.17	3.17	3.16	3.15	3.16	3.15	3.24	3.22	3.20	3.22	3.16	3.18	2.83	3.01	3.13	3.18
68.5	65.8	67.3	82.5	75.4	77.1	85.6	79.9	104.5	90.4	85.7	99.2	68.3	-	53.1	41.3	75.3
86.3	70.7	65.3	77.3	68.3	70.8	79.6	76.5	77.6	84.1	88.4	82.4	70.1	-	39.8	20.3	80.8

¹ Test Nr.

² Quellen f. feuerf. Ausgangsmat. (Gew.%)

SiC-Pulver³

AlN-Pulver³

⁴ Verb.d.Gruppe IIIa-Elements

Al₂O₃

SiO₂

Si₃N₄

⁵ Sinterbedingung.

⁶ Sintertemp. (°C)

⁷ Sinterzeit(h)

⁸ Atmosphäre

⁹ Eigensch.d.Sinterzeugn.

¹⁰ Dichte (g/cm³)

¹¹ Biegef. (kg/mm²)

¹² Raumtemp.

1400°C

key: 1-test no. 2-sources for refractory starting material (% by weight) 3-powder 4-compound of group IIIa element 5-sinter conditions 6-sinter temperature 7-sintering time 8-properties of sinter products 10-density 11-bending strength 12-room temp.

Table 2

<u>Tabelle 2</u>				
¹ Test Nr.	2	4	6	7
² Chemische Zusammensetzung (Gew.%)				
Al	8,5	12,4	3,3	6,1
N	3,2	5,8	0,8	1,2
O	1,5	2,2	0,8	1,2
Y	-	-	0,4	0,5

Key: 1-test no. 2-chemical composition (% by weight)

3344263

35.

FIGUR

Nummer

Int. Cl.

Anmeldetag:

Offenlegungstag:

33 44 263

C 04 B 35/56

7. Dezember 1983

28. Juni 1984



ORIGINAL PAGE, IS
OF POOR QUALITY

5 μ m

FIGUR 2



5 μ m